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TECHNOLOGY UTILIZATION REPORT

Technology Utilization Division

SUGGESTED METHOD FOR PLATING COPPER ON ALUMINUM

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNOLOGY UTILIZATION REPORT

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SUGGESTED METHOD FOR PLATING COPPER ON ALUMINUM

Prepared under contract for NASA
by Southwest Research Institute

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Foreword

The Administrator of the National Aeronautics and Space Administration has established a Technology Utilization Program for the rapid dissemination of information on technological developments that appear to be useful for industrial application. From a variety of sources, such as NASA research centers and NASA contractors, space-related technology is screened; and that which has potential industrial use is made generally available.

This publication is one of a series designed to provide such technological information. The report describes the successful application of the phosphate-anodizing process in copper plating commercially pure aluminum and several aluminum alloys; it also lists the advantages—as well as one disadvantage—compared with the zincate process in current use by industry. *EP.*

GEORGE J. HOWICK, DIRECTOR,
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Office of Technology Utilization

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Introduction

An investigation by James C. McConnell at Wallops Island Station determined that solid copper wire could be successfully soldered to aluminum that had been copperplated by the phosphate anodizing process. During tensile testing, the wire, in all cases, failed before any apparent damage to the plated sample or soldered joint was evident. During the tests it was suggested that thermal shock resulting from the soldering operation would cause blistering of the copperplate. Remarkably, no blistering occurred, and no evidence of plating separation showed in bend tests of the specimens.

Commercially pure aluminum was used in these tests; however, the process would be much more useful if extended to a variety of alloys. This would be especially true if the same anodizing solution were used for all alloys, since changing solutions from alloy to alloy becomes expensive. It would also have further industrial potential if the process could be used for a broader variety of plating compositions.

To confirm the results of the study and to supplement the available data with a variety of aluminum alloys and different plating compositions, a program was conducted at Southwest Research Institute (SRI) under the sponsorship of the Office of Technology Utilization of the National Aeronautics and Space Administration. The following report presents a detailed description of the procedure and the results.

Background

Electrodeposits of copper on any material are rarely used when durability or appearance is important. As a rule another metal, such as nickel, chromium, or silver, must be plated on a copper flash or plate. For instance, to plate chromium on aluminum or steel, a thin layer of copper is usually first plated on the part, fol-

lowed by a heavier plating of chromium for corrosion protection or appearance.

At present, the zincate process is used for most commercial electroplating on aluminum substrates. In this process a clean aluminum part is immersed in a strong alkali solution containing zinc salts. As the oxide dissolves, the aluminum is coated with a thin zinc film. The zinc film is then copperplated from a highly basic copper cyanide solution.

Several disadvantages of the zincate process are described by Spooner and Seraphim.* One major disadvantage is the tendency of the copperplate to blister or peel upon heating, as when copper is applied to a part or chassis that must have an electrical connection soldered to it. Another major disadvantage is metal removal during the zinc-coating part of the process. Parts with sharp corners or close tolerances, such as threaded parts, may be unusable because of metal removal caused by the highly basic zinc-coating procedure.

The new process is dependent on a closely controlled phosphate anodizing technique. The part to be plated is—

- (1) Cleaned and any oxide film removed
- (2) Phosphate anodized for 6 minutes in a 25-percent (by volume) phosphoric acid solution at 3 to 4 amperes per square foot at 15° C
- (3) Rinsed thoroughly in cold distilled water
- (4) Transferred immediately to a conventional acid copper-plating tank with power on and cathode agitation used (bright range predetermined by such tests as the Hull cell test)

The advantages of this process are the adherence of the coating to the aluminum substrate and its thick porous nature that aids in the plating bond. The one major disadvantage is that a high voltage, in the range of 60 to 90 volts

*R. C. Spooner and D. P. Seraphim, Phosphoric Acid Anodizing of Aluminum and Its Application to Electroplating, Trans. Inst. Metal Finishing, vol. 31, 1954, pp. 29-45.

depending upon the alloy of the substrate material, is required to maintain the current density during the anodizing process.

Procedure

Materials.—The materials used were 1100-H14, 2219-T87, 5052-0, 6061-T6, and 7106-T63. These were chosen as a representative sample of four alloy groups as well as commercially pure aluminum (1100). The 7106 alloy, still listed as an experimental material, is typical of commercial 7000-series alloys. In all cases the material thickness was 0.090 inch. Two industrial sand-cast aluminum alloys and one magnesium sample were also included. Because the magnesium was too reactive in the phosphoric acid, it was not extensively investigated. For the soldering tests a conventional rosin-core, tin-base solder was used with manual soldering techniques.

Surface preparation.—Sheets and castings in their as-received condition were cleaned by three different procedures:

- (1) Five percent hydrofluoric-acid bath
- (2) Concentrated sodium-hydroxide bath followed by a 25-percent nitric acid bath
- (3) Five percent hydrofluoric-acid bath preceded by abrasion with 600-grit silicon-carbide paper (for sheets only)

Phosphate-anodizing variables.—The variables studied included the anodizing solution's concentration, agitation, and temperature; the current density; and the time allowed. Two concentrations of phosphoric acid were used: (1) 25 percent solution of 87 percent phosphoric acid in distilled water, (2) 35 percent solution of 86 percent phosphoric acid in distilled water. Anodizing was performed with and without agitation at current densities of 5, 10, and 20 amperes per square foot, and the time varied from 2 to 10 minutes. The preliminary studies indicated that changes in the solution's temperature did not cause discernible variations in the anodized coating.

Copperplating.—Because the copperplating procedure (see fig. 1 for schematic) was not considered a variable, the parameters were held constant.

The electrolyte used was—

Copper sulfate (33 ounces per gallon)
Sulfuric acid (1.5 ounces per gallon)
Thiourea (0.0001 ounce per gallon)
Alconox (wetting agent) (0.027 ounce per gallon)

To cover the anodized surface before it dissolves, a high initial current must be used when plating. Therefore, a current density of 50 amperes per square foot was used for the first 2 minutes, followed by a current density of 10 amperes per square foot for 5 minutes. The specimens were then removed from the plating solution, washed in distilled water, and dried using alcohol and a hot-air blast.

Nickel plating.—To determine the feasibility of using the same anodizing pretreatment for plating nickel on aluminum, aluminum specimens were first cleaned in 5 percent hydrofluoric acid, phosphate-anodized as described on page 8 and nickel plated using the semibright process.

Evaluation

A detailed evaluation of both the plating and soldering procedures was made at SRI. As preparation for plating, three specimens (1 x 6 x 0.90 inch) were racked together and cleaned, using one of the methods previously described. The side of the specimen farthest from the cathode was then masked with a clear acrylic spray lacquer. The specimens were next connected electrically and immersed in the phosphate-anodizing solution as shown in figure 2. The cathode for the anodizing process was stainless steel of approximately the same size as the aluminum specimens.

After approximately 1-minute immersion, the current would begin to decrease. To maintain the predetermined amperage, the voltage was increased constantly for the next 3 to 4 minutes, in some cases to as high as 90 volts for a current density of 20 amperes per square foot on a 12-square-inch area. The voltage necessary to maintain a predetermined current was a function of the particular alloy, since alloy content affects conductivity as well as oxide-layer formation.

At the end of the anodizing period, the specimens were rinsed in distilled water. The rinsing procedure and the beginning of the plating

Figure 1.—Schematic of plating procedure.

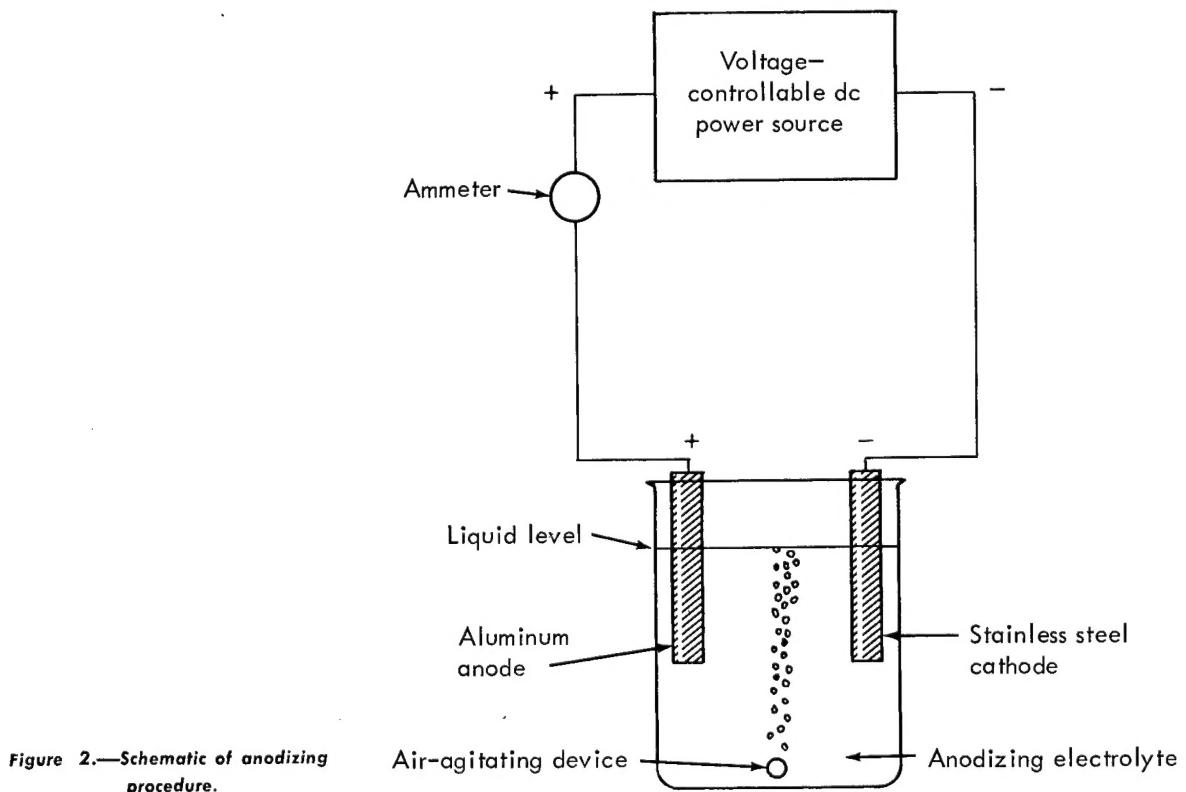
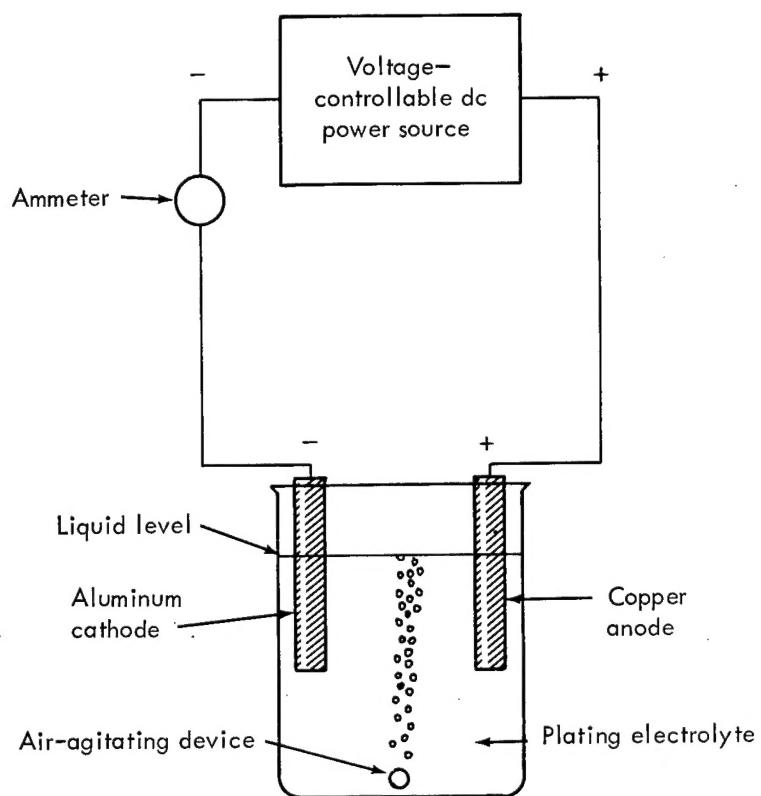


Figure 2.—Schematic of anodizing procedure.

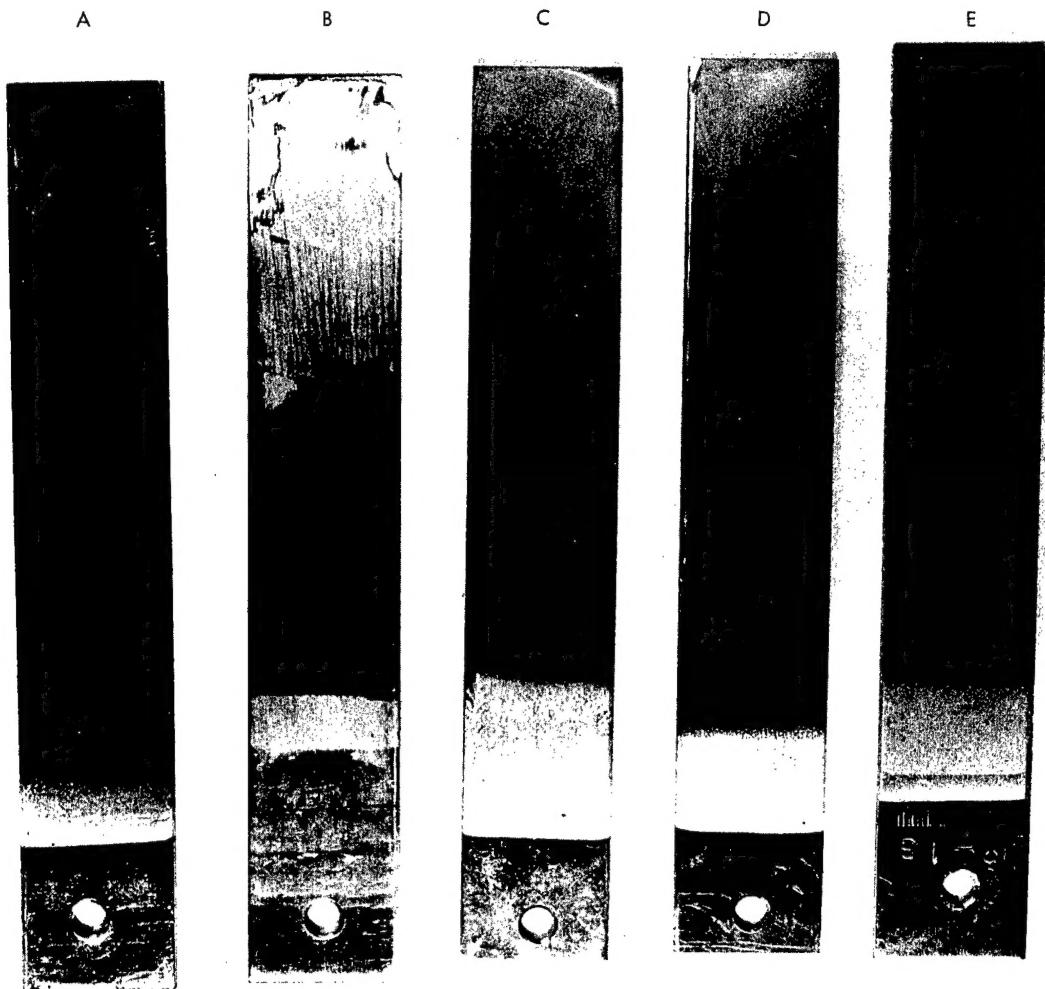


Figure 3.—Poor plating appearance due to (A) too violent agitation, (B) improper masking, (C, D) not having the power on when the specimen was transferred to the plating solution, and (E) "burning" caused by no agitation during anodizing.

process are crucial, since a mistake at this point will yield a poor plate.

First, the specimens must be thoroughly rinsed and kept moist. If the oxide coating is allowed to dry, the electrical conductivity of the oxide layer will be lowered to the extent that plating may be impossible. On the other hand, if the anodized specimens are allowed to remain in the water for more than about 15 minutes, a hydroxide will begin to form, filling the pores and adversely affecting the adhesion properties of the plating. Also, the specimens or parts must be connected electrically, and the power source must be on before the specimens are

immersed in the copper-plating solution. If this procedure is not followed, the oxide layer will be completely or partially dissolved by the plating solution and an uneven copper layer will result. (See fig. 3C and D.)

After plating, the sheet specimens underwent the following tests:

Bend test to a radius of 1 T (thickness).—Two bend tests of each material were made after plating, the results of which are illustrated in figures 4 through 8. The plating showed no evidence of flaking (figs. 4 through 7). The difference in ductility between the three alloys shown was responsible for the variation in bend

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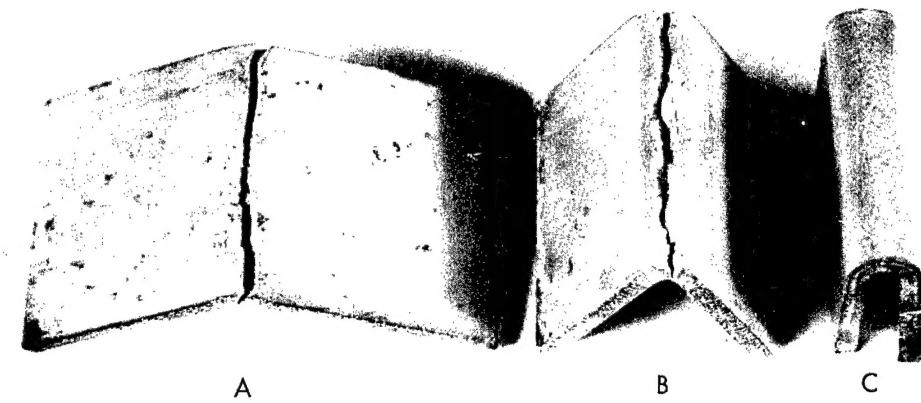


Figure 4.—Bend specimens showing integrity of plating on three alloys having different ductilities. (A) alloy 7106-T63, (B) alloy 6061-T6, and (C) alloy 1100-H14.



Figure 5.—1100-H14 bend specimen. This bend configuration is typical of ductile substrate material (1100-H14 and 5052-0).

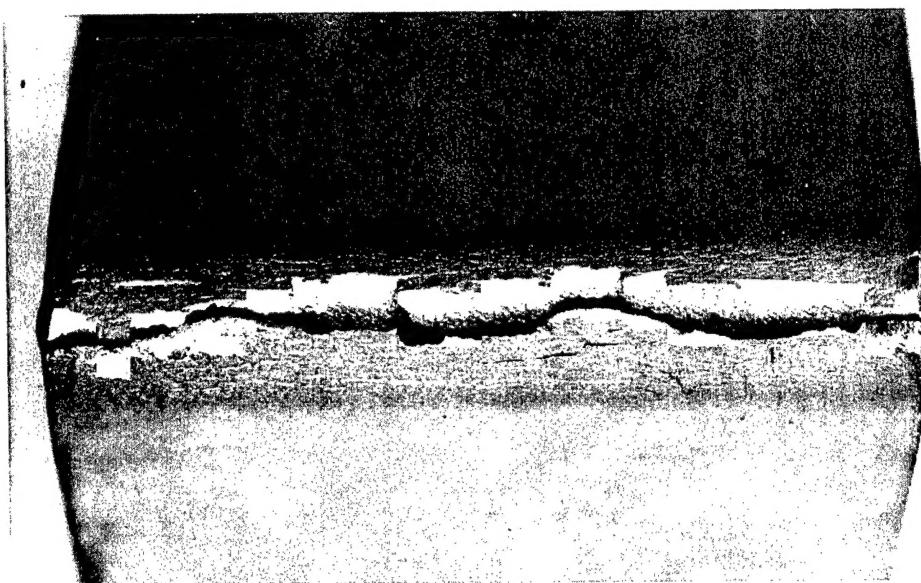


Figure 6.—6061-T6 bend specimen. This alloy has intermediate strength and ductility.

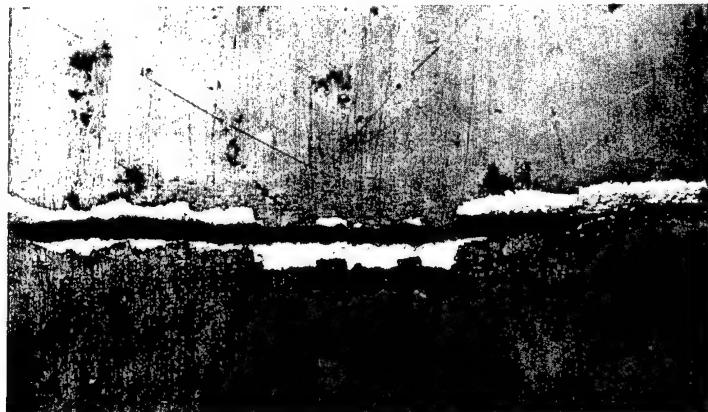


Figure 7.—7106-T63 bend specimen. This bend configuration is typical of brittle substrate material (7106-T63 and 2219-T87).

angle before failure. Additional bends were made of unplated stock to show that plating did not affect ductility. The 1-T bend radius was too sharp for the alloy with higher strength and lower ductility; however, it was satisfactory for indicating flaking resistance. Figures 5, 6, and 7 are enlarged views of the bends. Although checking of the alloy occurred, it did not flake. In figure 8 flaking is clearly visible adjacent to the crack. This bend test was intentionally made of a specimen (alloy 2219-T6) improperly cleaned before anodizing.

Baking test.—Figure 9 shows specimens representative of those baked at $350^{\circ}\text{ F} \pm 10^{\circ}$ for 30 minutes per AMS 2420. None of the specimens exhibited signs of flaking or blistering.

Tension tests of soldered joints.—Test specimens were soldered together to form a single shear joint (fig. 10C) with 60:40 tin-lead rosin-core solder. Approximately one-half inch of one end of each specimen was tinned; the two ends were then lapped and heated until they were joined. Results of the shear tests, using nominal parameters, are given in the table; averages are calculated from at least eight tests. Figure 10D shows a typical failure.

The plating on cast alloy specimens was

Tensile Load at Failure (lb)

Alloy	Average	High	Low
1100-----	1445	1825	1000
2219-----	920	1000	800
5052-----	1250	1475	1000
6061-----	1950	2300	1400
7106-----	2000	2500	1675

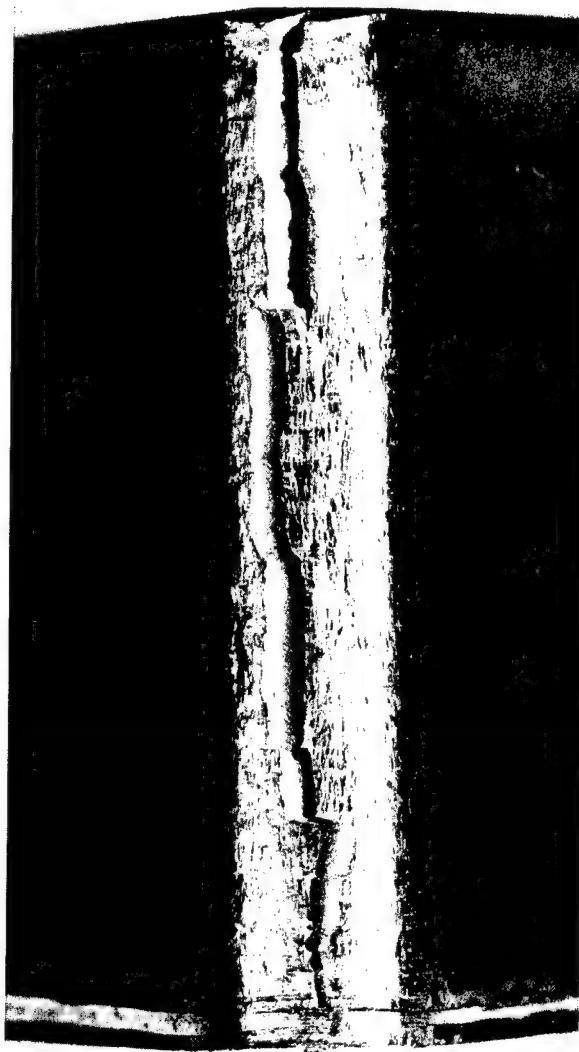


Figure 8.—Poor plating adhesion exhibited in this bend test is caused by improper cleaning before anodizing (2219-T6).



Figure 9.—Typical appearance of test strips after heating at 350° F for 30 minutes.

examined visually and found satisfactory. The form of the specimen is shown in figure 11. A soldering test was made to demonstrate the plating's adherence and wettability. The performance of this coating was identical to that observed on wrought aluminum alloys.

The results of these tests demonstrated the importance of controlling the various parameters of the anodizing operation. The important considerations for each step in the process are described below.

Surface preparation.—The literature for the



Figure 10.—(A) Aluminum strip, (B) after anodizing and plating, (C) soldered joint, and (D) joint after failure.

zincate process suggests that the optimum surface be clean and as smooth as possible. In this investigation, polishing specimens with 600-grit silicon carbide paper caused a slightly improved plating appearance, but did not appreciably increase the shear strength. Therefore, polishing aluminum parts at an additional cost should be restricted to removing corrosion products and stains. Because the caustic solution stained the copper-bearing alloy, its use was discontinued. The 5-percent hydrofluoric acid solution was sufficient to clean the speci-

mens in a reasonable time (3 to 5 minutes) and gave the most satisfactory results of the three preparations.

Anodizing.—A variety of anodizing parameters produced good results. Those parameters which gave the most consistent results with the alloys tested are listed below.

- (1) Anodizing solution: 35 percent of 86 percent phosphoric acid in distilled water
- (2) Anodizing current: 10 amperes per square foot
- (3) Anodizing time: 6 minutes
- (4) Anodizing solution temperature: room temperature (72° F to 76° F)

Solution agitation.—The agitation of the solution during anodizing is an important parameter. Violent agitation causes streaking (fig. 3A), but no agitation causes "burning" (fig. 3E). Consequently, the agitation rate, which will vary with bath size, work size, and geometry, must be determined for each application.

Plating.—Plating appearance and adhesion were excellent. No special precautions were necessary except those previously described.

Soldering results.—Soldering tests indicated that copper-plated aluminum or nickel-plated aluminum could be readily soldered by conven-

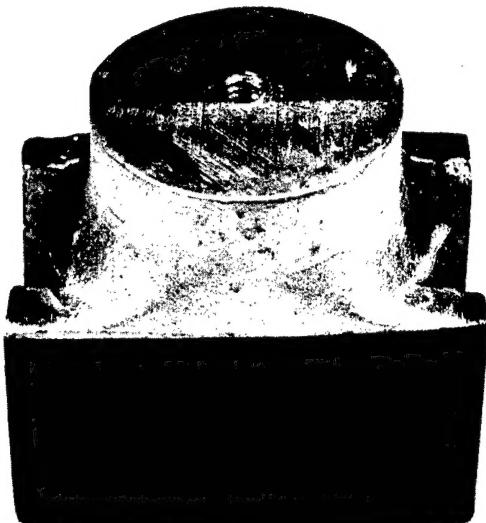


Figure 11.—Appearance of plated sand casting.

tional manual techniques. The solder readily wet the surfaces, and excellent shear test results were obtained.

Potential Industrial Applications

Among the potential industrial applications are:

- (1) Automotive products (bumper guards, tire molds, trim, pistons, and cylinders)
- (2) Electronic products (bus bars, switch gears, microwave fittings, and terminal boards)
- (3) Miscellaneous products (screws, nuts, bolts, window and door hardware, household appliances, jewelry, and beverage cans)

With the recent development of such high-

strength aluminum alloys as the 2219 and 7106 alloys studied during this program, items such as bumper guards, hydraulic parts, and small forgings could quite possibly be made of aluminum rather than of steel, which is now being used. These parts could be plated first with a flash of copper and then with decorative or hard chrome, whichever is applicable.

Commercial plants using large amounts of electricity have tried aluminum for bus bars but have discontinued it because of the problems encountered in connecting the bus bars. Bus bars joined by bolting or riveting have not proven satisfactory because of the buildup of corrosion products between the joints. However, the bus bars could be plated with copper by the phosphate-anodizing process and successfully joined by soldering.



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—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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